TITLE

# MOLDING MATERIAL

## CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation of co-pending International Patent Application No. PCT/GB02/02055 filed May 8, 2002, claiming priority to U.K. Patent Application No. 0111278.8 filed May 9, 2001 and to U.K. Patent Application No. 0130965.7 filed December 27, 2001. International Patent Application No. PCT/GB02/02055 was published as WO 02/090089 on November 14, 2002 in English under PCT Article 21(2).

## BACKGROUND OF THE INVENTION

The present invention relates to a molding material, particularly but not exclusively to a molding material comprising a uni-directional fibrous reinforcement material.

Composite molding materials comprise a resin material and a fibrous reinforcement material. The viscosity of the resin material is strongly influenced by the resin temperature. During processing, on heating the resin, the resin viscosity drops, allowing it to flow around the fibrous reinforcement material. However, as the resin material is heated beyond a certain point (activation temperature), the catalysts within it begin to react and the cross linking reaction of the resin molecules accelerates. The progressive polymerization increases the viscosity of the resin until it has passed a point beyond which it will not flow at all ('no flow point'). To further promote the flow of the resin material into the reinforcement material, pressure is applied to the molding formed from the composite molding material. Often, pressure is applied by the application of vacuum pressure to the molding.

Historically, molded articles or moldings were formed from a resin material either on its own or reinforced with a fibrous reinforcement material. Although the

products thus formed were satisfactory, it was difficult to guarantee the quality of the product due to the difficulty in controlling the ratio of the resin material to the fibrous reinforcement material. Another problem encountered in these materials was the entrapment of volatile gases during processing and curing of the material which caused voids in the cured laminate. The process was therefore refined such that the supplier of the resin provided the producer of the molded article with a preform or pre-fabricated molding material comprising reinforcement materials which were pre-impregnated with a resin material. These molding materials are known as prepregs.

The prepreg molding material allowed the fabricator to produce molded articles of a consistent quality. The prepreg material also enabled the fabricator to lay up a combined layer of reinforcement fibrous material and resin material at once.

A problem associated with prepreg materials is that voids occur in the cured product due to the presence of intralaminar and interlaminar gases which become trapped during processing of the prepreg material. The voids in molded products are roughly divided into two groups, namely intralayer voids which develop within respective prepreg layers due to the presence of intra-laminar gases and/or air (i.e. gases trapped within individual prepreg layers of a laminate structure), and interlayer voids which develop between prepreg layers due to the presence of inter-laminar gases (i.e. gases trapped between prepreg layers). The causes of the development of both interlayer voids and intralayer voids include volatile matters resulting from water and solvents contained in the prepreg resin, bubbles formed from air which has remained in the resin, etc. The predominant cause of interlayer voids is conceivably accumulated air which has been taken in between the prepreg layers during lamination and left behind there. This air is easily trapped between the tacky external surfaces of the prepreg layers during the lay-up of the prepreg. Such voids can result in the laminate having poor structural properties and can lead to premature failure of the composite material. Further, these voids result in a poor cosmetic quality finish of the cured product.

U.S. Patent No. 5,104,718 to Asada et al. discloses a unidirectionally paralleled fiber reinforced thermosetting resin prepreg having plural grooves arranged continuously in longitudinal direction on at least one side surface thereof. The grooves enable the passage of air during molding and, hence, no accumulation of interlaminar air occurs. Also, at the time of molding, the grooves serve as the passage of resin containing volatile matters and air and, together with the help of lateral shift of fibers surrounding the grooves, ultimately give a good molded product free from interlayer voids (see Col. 3, Lines 1 to 6). The material as disclosed in U.S. Patent No. 5,104,718 has several important disadvantages. The grooves only act as conduits to interlaminar gases and air. Intralaminar voids therefore still occur. Furthermore, as the grooves are located on the external surface of a prepreg layer, the grooves get clogged and thus blocked. Also, if too much pressure is applied on the prepreg layer during lay-up, the grooves distort which affects venting via the grooves. Also, if the grooves are too shallow or if they have the wrong shape, they get clogged immediately when a further prepreg layer is located thereon. If the groove is too deep, the prepreg has a lower lateral strength and is liable to tear. Also, the groove affects the cosmetic quality of the molding as it is present on the molded surface. Finally, the process of forming a grooved prepreg material is complicated and generally expensive as it requires an extra groove applying step after preimpregnation of the reinforcement material.

## SUMMARY OF THE INVENTION

We have discovered that the above problems can be largely reduced or overcome by a molding material comprising a layer of resin material and conjoined to at least one surface thereof a fibrous layer, the fibrous layer allowing entrapped laminar gases to pass out of the material during processing of the material. Upon curing of this breathable molding material, entrapped gases escape via the dry reinforcement layer, which prevents these voids from occurring. This material is

disclosed in more detail in WO 00/27632 (Ness et al.), which is incorporated herein by reference.

We have also discovered that the quality of the cured product depends on the processing conditions of the molding material. To process a breathable molding material, the processing conditions must be carefully controlled to prevent gases and air from being trapped in the material.

This is particularly important for breathable molding materials which comprise uni-directional fibrous reinforcement layers. In Fig. 1 of the drawings, a diagrammatic plan view is presented of a preform molding material 10 comprising a layer of a resin material 12 sandwiched between layers of a unidirectional fibrous reinforcement material 14. As the molding material starts to wet out during processing, areas 18 of the uni-directional fiber become trapped off or blocked by the resin 12 so that no air transport can occur in directions along the reinforcement fiber and perpendicular to the reinforcement fiber (x, y -direction and z -direction). Any residual laminar gases inside the fiber tows of the uni-directional material 14 get locked inside the tows 20 which results in interlayer and intralayer void areas in the cured product.

This problem can occur for a wide range of molding materials with both woven and unwoven reinforcement layers. However in woven and stitched venting (breathable) molding materials the problem occurs less frequently. Although we do not wish to be bound by any theory, we believe that both woven and stitched reinforcement material layers provide transport of gases within the plane of the reinforcement materials. Gases are therefore less likely to be trapped by the resin during processing of the material. However, the processing conditions of these materials must also be carefully controlled to prevent gas entrapment.

Problems of gas entrapment in molding materials with venting properties are particularly present during curing of molding materials which comprise one or more layers of a uni-directional fibrous reinforcement material or a non-uniform fibrous reinforcement material.

It is therefore desirable to provide an improved molding material and a method of forming said molding material for a more efficient fabrication of molded articles with a minimal void content, thereby addressing the above-described problems and/or which offers improvements generally.

In embodiments of the present invention, there are provided a molding material, a resin material, a method of manufacturing a molding material, a method of manufacturing a resin material and a molded article as defined in the accompanying claims.

In an embodiment of the invention, there is provided a preform multi-layered molding material comprising a layer of a reinforcement material and a layer of a resin material, the resin material layer comprising a first venting structure to allow interlaminar and intralaminar gases to pass out of said molding material via the reinforcement layer during processing. The resin layer thus acts as a conduit for both interlaminar gases and intralaminar gases which are conducted via the resin layer out of the material via the reinforcement layer. In this way, it is achieved that any entrapped interlaminar and intralaminar gases can escape via the resin material layer during processing of said material. Any entrapped gases can further escape from fiber tow to fiber tow via a transverse venting route formed by the venting structure. This also prevents the formation of interlaminar and intralaminar voids in the cured product.

In a further embodiment of the invention, the first venting structure may comprise passages or venting channels. These venting channels allow interlaminar and intralaminar gases to be conducted out of the molding material via these channels. The venting channels act as conduits for any gases within the resin layer and connect fibers in the reinforcement material via transverse venting routes from fiber to fiber. The conduits provide additional venting routes to any entrapped gases so that these gases can also escape from the molding material. The venting channels may extend over the full thickness of the resin material layer. During processing, as the reinforcement material is locally closed off by the resin material, the venting channels

connect these pockets to allow the gases to escape the molding material via the resin layer. This prevents entrapped gas pockets.

In an embodiment of the invention, the venting structure may be adapted to vent the resin layer in one or more directions. The venting structure may be adapted to be connected to a suitable gas extraction means. A suitable gas extraction means may comprise a vacuum pump in combination with vacuum consumables such as a vacuum bag, etc.

In another embodiment, the venting channels may extend substantially in a plane perpendicular to the resin layer. Preferably, the venting channels extend from one side of the resin layer across said layer through to the other side of the resin layer. The venting channels may further extend in a direction which is approximately parallel to the resin layer. In a preferred embodiment, the venting channels may extend from one side of the resin film across the resin film through to the other side of the resin film, whereby the end portions of the venting channels are offset relative to one another on either side of the resin layer so as to maximize the length and volume of the venting channel. This promotes the flow of any laminar gases and entrapped gases out of the molding material during processing. Preferably, the venting channels extend from one side of the resin layer across the resin layer to the other side of the resin layer in a zig-zag type fashion. This particular shape of the venting channels allows adequate venting of the areas closed off by the resin during processing, since the zig-zag type channels extend over an as large as possible volume within the resin layer.

In yet another embodiment of the inventions, the resin material layer may be discontinuous with the discontinuities forming the venting passages or channels. In a further embodiment of the invention the resin layer may comprise venting channels defined between lengthwise extending strips of resin material. The strips may extend in a non-linear lengthwise format. The resin strips may be at an approximate angle of $45^{\circ}$ or any other suitable angle relative to the direction of the fibers in the reinforcement layer. The strips may be arranged approximately parallel to one another.

In another embodiment of the invention, the first venting structure may comprise venting channels or passages which extend substantially in a plane parallel to the reinforcement layer. The venting structure may be formed by a discontinuous resin layer. The discontinuous resin layer may comprise patches, strips or small areas of resin which are located on the reinforcement material.

In a further embodiment of the inventions, the reinforcement layer may comprise a further venting structure for allowing gases to pass out of said molding material via the reinforcement layer during processing. The further venting structure may be formed by the reinforcement layer. The reinforcement material may be dry (unimpregnated by the resin) or at least partially dry (partially unimpregnated by the resin) to allow gases to be vented out via the reinforcement layer. In embodiments of the inventions, the molding material may comprise one or more resin layers and one or more reinforcement layers. The reinforcement material may be conjoined to the surface of the resin material so as to provide a substantially unimpregnated reinforcement layer.

In yet another embodiment of the inventions, there is provided a resin material comprising a venting structure for allowing gases to pass out of said resin material during processing of the material. The resin material may be in the form of a film or a layer. The resin film may be applied to any suitable reinforcement layer to form a molding material. The reinforcement material may comprise a non-woven reinforcement material such as a unidirectional non-woven reinforcement material. The reinforcement material may also comprise a woven reinforcement material. A further reinforcement material layer may be applied to the resin layer to form the molding material. In a preferred embodiment, the resin layer may be sandwiched between the reinforcement material layers.

In another embodiment of the invention, the reinforcement layers are held in place on the resin layer by the inherent tack of the resin material. This obviates the need for stitching, adhesive, or binder materials for keeping the molding material integral during transport and handling including lay-up. This property of the material

is particularly useful when the reinforcement material comprises non-woven reinforcement fibers, such as uni-directional fibers, as no stitching of the material is necessary which would otherwise affect the quality and mechanical properties of the molding material.

In an embodiment, the cosmetic surface quality of the molding material as hereinbefore described is high in comparison to conventional molding materials. The first venting structure and/or further venting structure may enable the resin material to completely wet the mold surface during processing whereby any entrapped air and laminar gases which may be located between the mold surface and the molding material can escape via the venting structure. Gases may thus escape via the venting structures as provided in the resin layer and/or the reinforcement layer.

In a further embodiment of the inventions, there is provided a method of forming or manufacturing a molding material as hereinbefore described. The method may comprise the steps of providing a resin material and a means for forming venting channels inside the resin material, the method further comprising the step of forming the venting channels in the resin material to form the gas permeable resin material. The method may further comprise the step of providing means for decreasing the viscosity of the resin material before the venting channels are formed so that the permeating means can permeate the resin material to form the venting channels.

In yet another embodiment of the invention, there is provided a method of forming or manufacturing a permeable resin film comprising the steps of providing a resin film, providing a heating means for increasing the temperature of said resin film thereby decreasing the viscosity of the resin, and providing a means for providing venting channels inside said resin film, said method further comprising the steps of increasing the temperature of said resin film below the temperature for processing the film and piercing said resin film to form said permeable resin film. The venting structure may be provided by piercing means, such as comb or needles or some other suitable means.

In an alternative embodiment, after heating and mixing, the resin material may be cast onto a suitable carrier means. Suitable carrier means may comprise a silicon coated carrier member, silicon backing paper, or a carrier member comprising a PTFE material. Since the resin film is still at a raised temperature after casting, a means may permeate the film to form a gas permeable resin film. The resin may also be located onto the carrier member as a discontinuous layer, for example in the form of strips of resin material.

In an embodiment of the inventions, a supply means may continuously supply a resin layer towards a venting means for making a gas permeable structure within the resin layer. The venting means continuously applies a venting structure in the resin layer. In a preferred embodiment, the resin film is continuously provided on a transport member, such as a conveyor belt, towards the venting member. The venting or piercing member, which is in contact with the resin film layer, is continuously movable in a direction perpendicular to the direction of travel of the resin film layer. In this way the venting structure is formed.

In a particular embodiment, the venting member comprises a comb which extends through the resin layer and which may be movable in a direction perpendicular to the direction of transport of the resin layer. The resin material is at a temperature whereby the viscosity of the resin is reduced and whereby no curing of the resin material occurs. The viscosity of the resin material is selected such that the viscosity is high enough to prevent the venting channel from closing due to the flow of the resin material, and the viscosity is low enough to prevent too much pressure from being exerted on the comb and to prevent the resin material from clogging the comb.

The resin film is preferably provided on a backing material to support the resin film during handling and application of the venting structure. The backing material may comprise a silicon paper. Alternatively, the resin material may be located on a conveyer belt, such as a PTFE belt, which supports the material during transport and handling.

In yet another embodiment of the invention, there is provided a method for forming a molding material comprising the steps of providing a layer of a permeable resin material, and providing a fibrous reinforcement layer, said method further comprising the steps of locating said reinforcement layer in relation to said permeable resin layer to form said molding material.

There is thus provided a molding material, a resin material, a method of manufacturing a molding material, a method of manufacturing a permeable resin material, and an article according to the embodiments of the invention.

We have discovered that molding materials with an air venting structure, and particularly air venting molding materials comprising layers of uni-directional reinforcement material, are difficult to process if the processing conditions cannot be carefully controlled. Air is then trapped inside the cured product.

We have discovered that by the creation of gaps which are located inside the reinforcement resin film, entrapped gases can be transported in both horizontal and vertical directions (in both a plane parallel to the resin layer and in a plane perpendicular to the plane of resin layer). The permeable resin film material with gaps or venting channels can be applied as a resin layer to any molding material and to any other composite materials to enable or improve venting of interlaminar and intralaminar gases.

Preferably, the permeable reinforcement resin material is applied to molding materials comprising unidirectional reinforcement layers, since these layers are generally difficult to process due to air blocks or traps which can occur in the unidirectional fibrous layers.

We have also discovered that the molding material as hereinbefore described has a better cosmetic surface quality in comparison to conventional molding materials. The venting structure improves venting of air, interlaminar and intralaminar gases. This enables the resin to completely wet out the mold surface during processing. Upon curing, this results in the enhanced cosmetic surface quality.

Venting of the molding material can further be improved by a discontinuous resin layer. The resin layer may comprise discontinuous strips or areas of a resin material. This greatly enhances venting of the molding material during processing and promotes flow of the resin material. This prevents the problem of trapped venting paths from occurring.

The preform molding material as hereinbefore described has the advantage that it prevents both intralayer voids and interlayer voids from occurring. This results in a void-free molded product of a superior mechanical and cosmetic quality. The preform molding material is dry to touch which simplifies handling of the material in comparison with conventional prepregs. Furthermore, since the first and further venting structures are situated within the molding material, the structures are robust and not affected by accidental clogging or blockage. Also, the molding material is cost-effectively and production is uncomplicated.

The preform multi-layered molding material preferably comprises a layer of a resin material sandwiched between layers of reinforcement material. The reinforcement material comprises a further venting structure. The molding material is easy to handle due to the absence of resin on the external surface of the material. If locally external surface tack is necessary, for example for applying the molding material on a vertical surface or standing part of the mold or molding, local pressure is applied to the material so as to locally impregnate the reinforcement material. In this way, local areas of the material are provided with external surface tack.

Various objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description of the preferred embodiment, when read in light of the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 presents a conventional molding material comprising unidirectional fibers (UD molding material) in a diagrammatic plan view.

Fig. 2 presents a diagrammatic perspective view of a molding material according to an embodiment of the invention.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The molding material 10 comprises a layer of a resin material 12 sandwiched between layers of unidirectional fibrous reinforcement material 14, whereby the reinforcement material 14 is conjoined to the surfaces of the resin material 12. As shown in Fig. 1, as the molding material 10 is processed and the reinforcement material 14 starts to be wetted out by the resin 12, the resin 12 tracks through gaps in the reinforcement material first, and areas 18 of the uni-directional fiber 14 become trapped off or blocked 20 so that no air transport can occur in directions 22 along the reinforcement fiber and perpendicular to the reinforcement fiber (x, y -direction and z -direction). Any residual laminar gases inside the fiber tows get locked inside the tows, which creates void areas in the cured product.

The preform molding material 100 comprises a first and a second layer of a reinforcement material 102,104 comprising multiple uni-directional fiber tows 112, and a layer of a resin material 106 arranged between the reinforcement layers 102, 104. The resin material layer 106 comprises a first venting structure to allow gases to pass out of said molding material 100 via the reinforcement layer 102,104 during processing. The first venting structure comprises venting channels or breaks in the resin film 108 which extend substantially in a plane perpendicular to the resin layer 106. The venting channels 108 also extend in a direction which is approximately parallel to the resin layer 106. In this way, the venting channels can extend in a zig-zag type fashion. This increases the volume of the channels, which promotes the gas venting properties of the resin layer. The venting channels or resin breaks 108 create air flow in x, y and z-direction 110 from fiber tow 112 to fiber tow 112. Since the reinforcement material layers 102,104 are essentially dry, the reinforcement layers 102,104 comprise a further venting structure formed by the fiber tows to allow gases to pass out of said molding material 100 via the reinforcement layers 102,104 during

processing. The venting channels 108 provide transverse connections in the reinforcement material 102,104 to reconnect closed off areas of the reinforcement material during processing to allow venting of entrapped gases out of the molding material.

In use, the molding material 100 is processed in the usual way by increasing the temperature of the resin material 106. Further, a vacuum pressure may be applied over the molding material 100 to promote the evacuation of gases, such as air, from the molding material 100 and to generally promote the flow of the reinforcement resin material 106 into the fibrous reinforcement material 102,104. The vacuum is applied by locating the laminate structure within an enclosure, such as a vacuum bag, and subsequently a proportion of the air is removed from the enclosure.

During processing, the resin material 106 impregnates the fibrous material 102,104 whereby any entrapped air can escape, both in X-Y directions parallel to the plane of the reinforcement material and perpendicular thereto in the Z direction. This is possible due to the venting channels 108 which are located within the resin film material 106. The venting channels then close as resin infusion into the reinforce material continues and the molding material is further processed. This results in a cured product which is essentially void-free, thereby obviating the problems which were discussed hereinbefore and which are presented in Fig. 1 of the drawings.

In accordance with the provisions of the patent statutes, the principle and mode of operation of this invention have been explained and illustrated in its preferred embodiment. However, it must be understood that this invention may be practiced otherwise than as specifically explained and illustrated without departing from its spirit or scope. For example, the order in which the steps of the method of this invention may be varied from that specifically described above.